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(54) Title: SINGLE REACTOR BIMODAL HMW-HDPE FILM RESIN WITH IMPROVED BUBBLE STABILITY

(57) Abstract

Single reactor bimodal MWD high molecular weight polyethylene film resin has improved bubble stability. The bimodal molecular weight distribution resin has low resin elasticity. Preferably the resin is made catalytically in one reactor. The preferred catalyst appears to control the properties of bubble stability and elasticity.

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SINGLE REACTOR BIMODAL HMW-HDPE FILM RESIN
WITH IMPROVED BUBBLE STABILITY

Increasing the molecular weight of polyethylene (and
copolymers of ethylene) generally results in enhancing
tensile strength, ultimate elongation, impact strength,
puncture resistance, and toughness, of films produced
5   therefrom. However, increasing the molecular weight of the
polyethylene will usually decrease its processability. By
providing a high molecular weight polyethylene with a lower
molecular weight component, the desirable characteristics
due to the high molecular weight component can be retained
10   while improving processability of the mixture containing
the high molecular weight component. To produce such
mixtures, various alternatives are being considered,
including post reactor or melt blending, catalysis in a
single reactor with a catalyst effective to produce such a
15   product and lastly use of multistage reactors, in which
diverse average molecular weight components can be produced
in each reactor. In accordance with the invention, the
bubble stability of resins produced far surpass those
produced by other mixed metal catalyst(s).

20   In accordance with the invention, a resin of broad or
bimodal molecular weight distribution has been produced
catalytically in a single reactor. Moreover, improvement
in bubble stability of the resin during film production
over other bimodal molecular weight resins has been
25   attributed to the new resins herein. Bubble stability is
relevant to upstream processing in high stalk extrusion
equipment. This improvement in bubble stability has been
correlated to resin elasticity; and each property appears
to be catalyst controlled.

30   The figure is a graph in which the elasticity (G'/G")
is plotted against low shear viscosity (@ 0.1 sec.$^{-1}$)

In accordance with the invention, resins of broad or
bimodal molecular weight distribution have been produced in

a single reactor; these may be ethylene polymers and/or copolymers. By the phrase "bimodal molecular weight distribution" we mean two components of different molecular weights, accordingly one having a higher relative molecular

5   weight than the other of the two components. Improvement in bubble stability of the resin during film production over other bimodal molecular weight resins has been attributed to the new resins herein. The resins which are processed on high stalk extrusion lines exhibit excellent

10   bubble stability, a prerequisite to being processed on those lines. This improvement in bubble stability has been correlated to resin elasticity; and each property appears to be directly a result of the catalyst used to make them.

The resin of this invention may be either 1) a

15   homopolymer of ethylene; 2) at least one copolymer of a preponderance i.e., greater than 50 wt.% of ethylene with a minor amount of a 1-olefin containing 3 to 10 carbon atoms, preferably a 1-olefin containing 4 to 10 carbon atoms, e.g., 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-

20   octene, 1-decene, and mixtures thereof; or 3) a mixture of any of the foregoing polymers. In general, the polymer product will comprise an amount of polymerized comonomer which is in the range, for example, of 0 to 30 weight percent, based on the total weight of polymer.

25   The resins produced herein have a density (measured by ASTM D 1505) in the range of 0.89 to 0.970. The resins which can be produced in accordance with the invention can exhibit densities of high density, medium density or low density resins, respectively. Accordingly, the resins can

30   be produced which exhibit specific density in the range of 0.89 to .929 [low density], 0.930 to .940 [medium density], and .940 to .970 [high density.]

The resins of the invention exhibit a characteristic elasticity. It is believed that th elasticity of the

35   products we produce is a critical factor in determining the

bubble stability of HMW resins. We measure bubble
stability in terms of our ability to make thin films (1
mil) at (120 lbs/hr) commercial output rates. When the
resin has high elasticity any small disturbances during
film blowing are amplified resulting in an uncontrollable
process. The combination of low elasticity and high
viscosity of the invention resins allows disturbances
during film blowing to be effectively damped out.

The dynamic elasticity of the polymer product of the
invention is no higher than 0.65 at 0.1 rad./sec. at a
corresponding complex viscosity of no higher than 20E5 (20
x 10^5 poises) at 0.1 rad./sec., preferably 0.45 to 0.58 at
a corresponding complex viscosity of 6E5 to 20E5, and most
preferably 0.45 to 0.52 at a corresponding complex
viscosity of 7E5 to 14E5.

The dynamic elasticity as used herein is defined as
the ratio of the storage modulus $G'(w)$ to the loss modulus
$G''(w)$. The storage modulus $G'(w)$, and the complex
viscosity are defined in ASTM D 4440-84. The properties
were measured accordingly at 200°C.

The resins of the invention comprise a HMW component
and a LMW component with a high molecular weight (HMW)
component weight fraction which is greater than 0 (zero).
Generally, the HMW component weight fraction can be
controlled within a very broad range, while maintaining
excellent properties in ultimate applications, such as film
production. The weight fraction of HMW component can range
from .01 to .99, preferably from .4 to .7 and most
preferably from .5 to .6. The resin has a molecular weight
distribution, which is characterized as MFR or Mw/Mn. The
MFR of resin products of the invention can range from 20 to
300, preferably from 60 to 200, and most preferably from 80
to 150. The Mw/Mn of resin products of the invention can
range from 2.5 to 60, pr ferably from 10 to 40, and most
preferably from 15 to 30.

The low molecular weight component of resin product of
the invention is much narrower in molecular weight
distribution, than that produced by a conventional Ziegler
Natta catalyst containing only one transition metal such as
5   titanium and/or that produced by a conventional tandem two-
reactor process. The narrow MWD of the LMW component is a
result of the single site metallocene catalyst component.
This narrower molecular weight distribution of the low
molecular weight component of the resin of the invention
10   may be responsible for the reduced tendency towards die-lip
buildup and smoking because of the absence of very low
molecular weight tails. In preferred embodiments, the M_w/M_n
of the low molecular weight component is less than 3
whereas the high molecular weight component is
15   characterized by M_w/M_n greater than 3.   That narrower
distribution also enables production of much lower
molecular weight component, as the LMW component, without
encountering the die-lip buildup problem.

The compositions of the invention can be extruded into
20   pipes and injection or blow molded into articles or
extruded and blown into films. Films can be produced which
are 0.2 to 10.0 mils, preferably 0.5 to 2.0 mils,
thickness. For commercial applications, blown films
preferably have an FQR value of less than 50; FQR (film
25   quality rating) relates to film gels. Lower FQR values
reflect lower gels and thus are preferred. Blow molded
articles include bottles, containers, fuel tanks and drums.

For film production, the products may contain any of
various additives conventionally added to polymer
30   compositions such as lubricants, microtalc, stabilizer,
antioxidants, compatibilizers, pigments, etc. These
reagents can be employed to stabilize the products against
oxidation. For example, additive packages comprising 400-
1200 ppm hindered phenol(s); 200-2000 ppm phosphit s; 250
35   to 1000 ppm antistats and 250-2000 ppm stearat s, for

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addition to the resin powders, can be used for
pelletization. The polymers can be added directly to a
blown film extruder, e.g., an Alpine extruder, to produce
films having a thickness, for example of 0.2 to 5 mils.

5   The following Examples further illustrate the
essential features of the invention. However, it will be
apparent to those skilled in the art that the specific
reactants and reaction conditions used in the Examples do
not limit the scope of the invention.

10   The properties of the polymers produced in the
Examples were determined by the following test methods:

Density	ASTM D-1505 - a plaque is made and conditioned for one hour at 100°C to approach equilibrium crystallinity. Measurement for density is then made in a density gradient column; reported as gms/cc.
Melt Index (MI), I_2	ASTM D-1238 - (190°C/2160 g) Measured at 190°C - reported as grams per 10 minutes.
High Load Melt Index (HLMI), I_{21} or FI	ASTM D-1238 - (190°C/21600 g) Measured at 10 times the weight used in the melt index test above.
Melt Flow Ratio (MFR)	$\dfrac{I_{21}}{I_2}$

The ethylene polymer product of this invention is
capable of being formed into thin gauge films, e.g., of up
30   to 10 mils., of superior mechanical properties, e.g., an
Elmendorf tear resistance in the machine direction (MD
Tear, ASTM D1922) of at least 10 g/mil, preferably 15 to 60
g/mil, and more preferably 20 to 60 g/mil, and a Dart Drop
Impact resistance (F_{50}, ASTM D1709) of at least 200 g,
35   preferably 200 to 600 g, and more preferably 250 to 600 g.

When the resin is made with the preferred catalyst described below it will contain 0.5 to 20 ppm of transition metals. In particularly preferred embodiments described herein the resin will contain 0.1 to 10 ppm Zr and 0.5 to 10 ppm Ti. The as formed reactor product is granular and has a preferred average particle size range of 0.01 - .04 inches.

Process for Production of Resins

Preferably, the resins of the invention are made catalytically in one reactor, under reactor conditions described below. Preferably, they are made in the presence of catalyst comprising two sources of transition metal which exhibit different hydrogen response, one from the other, in polymerization of ethylene conducted in the presence of hydrogen. Preferably, the catalyst is supported and comprises 0.1 - 5.0 weight percent, preferably 0.3 to 3.0, and most preferably 0.5 to 1.5 wt.% of titanium and 0.05 to 1.0 wt.%, preferably 0.1 to 0.8, and most preferably 0.20 to 0.50 wt.% percent of zirconium. The preferred catalysts are described below.

In the polymerizations, the gaseous monomer feed may consist wholly of ethylene or may comprise a preponderance of ethylene and a minor amount of a comonomer such as a 1-olefin containing 3 to 10 carbon atoms. Comonomeric 1-olefins which may be employed are, for example, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, and mixtures thereof. The comonomer may be present in the monomeric compositions.

The amount of comonomer may be in the range, for example, of 0 to 30, preferably 0 to 20 weight percent, based on the total weight of polymer produced in the process.

Hydrogen is fed to the reactor. Hydrogen is fed to the reactor such that the molar ratio of hydrogen to

ethylene (H_2/C_2 ratio) is, for example, up to 0.04, preferably .005 to 0.015.

The ethylene partial pressure employed in the reactor is no higher than 250 psia, for example in the range of 150 to 200 psia, preferably in the range of 170 to 190 psia.

If desired for any purpose, e.g., to control superficial gas velocity or to absorb heat of reaction, an inert gas such as nitrogen may also be present in one or both reactors in addition to the monomer and hydrogen. Thus the total pressure in both reactors may be in the range, for example, of 100 to 600 psig, preferably 200 to 350 psig.

The temperature of polymerization in the reactor may be in the range, for example, of 60 to 130°C, preferably 70 to 100°C. The residence time of the catalyst in the reactor is 1 to 8 hours, preferably 2 to 4 hours in the reactor.

The productivity of the process in the reactor in terms of grams of polymer per gram of catalyst, may be in the range, for example, of 1,000 to 10,000g/g, preferably 1,500 to 8,000 g/g; The foregoing ranges are based on analysis of residual catalyst metals in the resin product.

The amount of cocatalyst utilized together with the preferred catalyst employed in the process of making the products of this invention whether for pre-reduction or activation of the catalyst prior to polymerization or added to the reactor is generally in the range, for example, of 0 to 100 gram atoms of cocatalyst metal, e.g., aluminum, per gram atom of transition metal, e.g., titanium, preferably 5 to 50 gram atoms of cocatalyst metal per gram atom of transition metal.

The catalysts, preferred at this time, for producing the bimodal molecular weight distribution resins of the invention, are made in accordance with the S.N.08/151,664 filed November 15, 1993 and are described here:

Catalyst Composition

Catalysts which contain at least two transition
metals, one in the form of a metallocene and one transition
metal in the form of a non-metallocene, have an activity of
5   at least 1000 g polymer/g catalyst or 100 kg polymer/g of
each transition metal.

The catalysts of the invention comprise a cocatalyst
comprising an aluminum alkyl compound, such as a trialkyl
aluminum, free of alumoxane and free of water, or oxygen-
10   containing oligomers and polymers of the aluminum alkyl
compound, and a catalyst precursor comprising a carrier,
an alumoxane and at least one metallocene; in one
embodiment the catalysts further include a non-metallocene
transition metal source.

15   The carrier material is a solid, particulate, porous,
preferably inorganic material, such as an oxide of silicon
and/or of aluminum. The carrier material is used in the
form of a dry powder having an average particle size of
from 1 micron to 500 microns, preferably from 10 microns to
20   250 microns. The surface area of the carrier is at least
about 3 square meters per gram (m^2/g), and preferably at
least 50 m^2/g up to 350 m^2/g. The carrier material should
be dry, that is, free of absorbed water. Drying of the
carrier material can be effected by heating at 100°C to
25   1000°C, preferably at 600°C. When the carrier is silica,
it is heated to at least 200°C, preferably 200°C to 850°C
and most preferably at 600°C. The carrier material must
have at least some active hydroxyl (OH) groups to produce
the catalyst composition of this invention.
30   In the most preferred embodiment, the carrier is
silica which, prior to the use thereof in the first
catalyst synthesis step, has been dehydrated by fluidizing
it with nitrogen and heating at 600°C for 16 hours to
achieve a surface hydroxyl group concentration of 0.7
35   millimoles per gram (mmols/g). The silica of the most
preferred embodiment is a high surface area, amorphous

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silica (surface area = 300 m^2/g; pore volume of 1.65 cm^3/g),
and it is a material marketed under the tradenames of
Davison 952 or Davison 955 by the Davison Chemical Division
of W.R. Grace and Company. The silica is in the form of
5   spherical particles, e.g., as obtained by a spray-drying
process. As procured, these silicas are not calcined; and
this must be dehydrated, as indicated above.

The catalyst synthesis is undertaken under inert
conditions, in the absence of water and of oxygen. The
10   carrier is dispersed in solvent to form a slurry.

The carrier material, having said (OH) groups, is
slurried in a non-polar solvent and the resulting slurry is
contacted with at least one organomagnesium compound having
the empirical formula below. The slurry of the carrier
15   material in the solvent is prepared by introducing the
carrier into the solvent, preferably while stirring, and
heating the mixture to 25 to 70°C, preferably to 40 to
60°C. Temperatures here are critical with respect to the
non-metallocene transition metal which is subsequently
20   added; that is temperatures in this slurry of 90°C result
in deactivation of the transition metal added subsequently.
Accordingly, all catalyst precursor synthesis steps are
conducted below 90°C. The slurry is then contacted with
the aforementioned organomagnesium compound, while the
25   heating is continued as indicated.

The organomagnesium compound has the empirical formula
$$R_m \; Mg \; R'_n$$
where R is an alkyl of 1 to 12 carbon atoms, and generally
where R and R' are the same or different C_2-C_{12} alkyl
30   groups, preferably C_4-C_{10} alkyl groups, more preferably C_4-C_8
alkyl groups, and most preferably both R and R' are mostly
butyl groups, and m and n are each 0, 1 or 2, providing
that m + n is equal to the valence of Mg.

Suitable non-polar solvents are materials in which all
35   of the reactants used herein, i.e., the organomagnesium

compound, and the non-metallocene transition metal
compound, are at least partially soluble and which are
liquid at reaction temperatures. Preferred non-polar
solvents are alkanes, such as isopentane, hexane, n-
5   heptane, octane, nonane, and decane, although a variety of
other materials including cycloalkanes, such as
cyclohexane, aromatics, such as benzene, toluene and
ethylbenzene, may also be employed. The most preferred
non-polar solvent is isopentane. Prior to use, the non-
10   polar solvent should be purified, such as by percolation
through silica gel and/or molecular sieves, to remove
traces of water, oxygen, polar compounds, and other
materials capable of adversely affecting catalyst activity.
       In the most preferred embodiment of the synthesis of
15   this catalyst it is important to add only such an amount of
the organomagnesium compound that will be deposited -
physically or chemically - onto the support since any
excess of the organomagnesium compound in the solution may
react with other synthesis chemicals and precipitate
20   outside of the support. The carrier drying temperature
affects the number of sites on the carrier available for
the organomagnesium compound - the higher the drying
temperature the lower the number of sites. Thus, the exact
molar ratio of the organomagnesium compound to the hydroxyl
25   groups will vary and must be determined on a case-by-case
basis to assure that only so much of the organomagnesium
compound is added to the solution as will be deposited onto
the support without leaving any excess of the
organomagnesium compound in the solution. Furthermore, it
30   is believed that the molar amount of the organomagnesium
compound deposited onto the support is greater than the
molar content of the hydroxyl groups on the support. Thus,
the molar ratios given below are intended only as an
approximate guideline and the exact amount of the
35   organomagnesium compound in this embodiment must be

controlled by the functional limitation discussed above,
i.e., it must not be greater than that which can be
deposited onto the support. If greater than that amount is
added to the solvent, the excess may react with the non-
5   metallocene transition metal compound, thereby forming a
precipitate outside of the support which is detrimental in
the synthesis of our catalyst and must be avoided. The
amount of the organomagnesium compound which is not greater
than that deposited onto the support can be determined in
10   any conventional manner, e.g., by adding the
organomagnesium compound to the slurry of the carrier in
the solvent, while stirring the slurry, until the
organomagnesium compound is detected as a solution in the
solvent.
15   For example, for the silica carrier heated at 600°C,
the amount of the organomagnesium compound added to the
slurry is such that the molar ratio of Mg to the hydroxyl
groups (OH) on the solid carrier is 0.5:1 to 4:1,
preferably 0.8:1 to 3:1, more preferably 0.9:1 to 2:1 and
20   most preferably 1:1. The organomagnesium compound
dissolves in the non-polar solvent to form a solution from
which the organomagnesium compound is deposited onto the
carrier.
It is also possible to add such an amount of the
25   organomagesium compound which is in excess of that which
will be deposited onto the support, and then remove, e.g.,
by filtration and washing, any excess of the
organomagnesium compound. However, this alternative is
less desirable than the most preferred embodiment described
30   above.
The organomagnesium treated support is contacted with
an organic alcohol reagent (ROH) containing RO- groups
which are reactive or capable of displacing alkyl groups on
the magnesium. The amount of this organic alcohol reagent
35   is effective to provide a ROH:Mg ratio of 0.5 to 2.0,
preferably 0.8 to 1.5.

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     Contact of the silica supported magnesium compound, with the organic alcohol reagent is undertaken in the slurry. Contact is undertaken at a temperature ranging from 25°C to 80°C, preferably 40°C to 70°C.

5   The alkyl group in the organic alcohol reagent can contain 1 to 12 carbon atoms, preferably 1 to 8; in the embodiments below, it is an alkyl containing 2 to 4 carbon atoms, particularly of 4 carbon atoms (butyl). The inclusion of the alcohol reagent step in the catalyst

10 synthesis of the invention produces a catalyst which, relative to the absence of this step, is much more active, requires much less non-transition metal (e.g. titanium), and is much more active with respect to the product component produced with the metallocene-transition metal

15 component. In addition, the alcohol addition step is required in order to provide a final catalyst that will produce bimodal MWD resin with excellent bubble-stability during the film-forming process.

     After the addition of the organic alcohol reagent to

20 the slurry is completed, the slurry is contacted with a non-metallocene transition metal compound, free of substituted or unsubstituted cyclopentadienyl groups. The slurry temperature must be maintained at 25 to 70°C, preferably to 40 to 60°C. As noted above, temperatures in

25 this slurry of 80°C or greater result in deactivation of the non-metallocene transition metal. Suitable non-metallocene transition metal compounds used herein are compounds of metals of Groups 4A, and 5A, of the Periodic . Chart of the Elements, as published by Chemical and

30 Engineering News, 63(5), 27, 1985, providing that such compounds are soluble in the non-polar solvents. Non-limiting examples of such compounds are titanium and vanadium halides, e.g., titanium tetrachloride, $TiCl_4$, vanadium tetrachloride, VCl_4, vanadium oxytrichloride,

35 $VOCl_3$, titanium and vanadium alkoxides, wher in the alkoxide moiety has a branched or unbranched alkyl radical

of 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms.
The preferred transition metal compounds are titanium
compounds, preferably tetravalent titanium compounds. The
most preferred titanium compound is titanium tetrachloride.
5   The amount of titanium or vanadium, in non-metallocene form
ranges from a Ti/Mg molar ratio of 0.3 to 1.0, preferably
from 0.50 to 0.80.

Mixtures of such non-metallocene transition metal
compounds may also be used and generally no restrictions
10   are imposed on the transition metal compounds which may be
included. Any transition metal compound that may be used
alone may also be used in conjunction with other transition
metal compounds.

After the addition of the non-metallocene transition
15   metal compound is complete, the slurry solvent is removed
by evaporation or filtering to obtain a free-flowing
powder. Next, incorporation of the metallocene can be
undertaken. The metallocene is activated with an
alumoxane.

20   The metallocene compound has the formula $Cp_xMA_yB_z$ in
which Cp is an unsubstituted or substituted
cyclopentadienyl group, M is zirconium or hafnium and A and
B belong to the group including a halogen atom, hydrogen or
an alkyl group. In the above formula of the metallocene
25   compound, the preferred transition metal atom M is
zirconium. In the above formula of the metallocene
compound, the Cp group is an unsubstituted, a mono- or a -
polysubstituted cyclopentadienyl group: and x is at least
1. The substituents on the cyclopentadienyl group can be
30   preferably straight-chain C_1-C_6 alkyl groups. The
cyclopentadienyl group can be also a part of a bicyclic or
a tricyclic moiety such as indenyl, tetrahydroindenyl,
fluorenyl or a partially hydrogenated fluorenyl group, as
well as a part of a substituted bicyclic or tricyclic
35   moiety. In the case when x in the above formula of the
metallocene compound is equal to 2, the cyclopentadienyl

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groups can be also bridged by polymethylene or
dialkylsilane groups, such as $-CH_2-$, $-CH_2-CH_2-$, $-CR'R''-$ and
$-CR'R''-CR'R''-$ where R' and R'' are short alkyl groups or
hydrogen, $-Si(CH_3)_2-$, $Si(CH_3)_2-CH_2-CH_2-Si(CH_3)_2-$ and similar
5   bridge groups. If the A and B substituents in the above
formula of the metallocene compound are halogen atoms, they
belong to the group of fluorine, chlorine, bromine or
iodine; and y + z is 3 or less, provided that x + y + z
equals the valence of M. If the substituents A and B in
10   the above formula of the metallocene compound are alkyl
groups, they are preferably straight-chain or branched C_1-C_8
alkyl groups, such as methyl, ethyl, n-propyl, isopropyl,
n-butyl, isobutyl, n-pentyl, n-hexyl or n-octyl.
      Suitable metallocene compounds include
15   bis(cyclopentadienyl)metal dihalides,
bis(cyclopentadienyl)metal hydridohalides,
bis(cyclopentadienyl)metal monoalkyl monohalides,
bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal
dihalides wherein the metal is zirconium or hafnium, halide
20   groups are preferably chlorine and the alkyl groups are C_1-
C_6 alkyls. Illustrative, but non-limiting examples of
metallocenes include bis(cyclopentadienyl)zirconium
dichloride, bis(cyclopentadienyl)hafnium dichloride,
bis(cyclopentadienyl)zirconium dimethyl,
25   bis(cyclopentadienyl)hafnium dimethyl,
bis(cyclopentadienyl)zirconium hydridochloride,
bis(cyclopentadienyl)hafnium hydridochloride, bis(n-
butylcyclopentadienyl)zirconium dichloride, bis(n-
butylcyclopentadienyl)hafnium dichloride, bis(n-
30   butylcyclopentadienyl)zirconium dimethyl, bis(n-
butylcyclopentadienyl)hafnium dimethyl, bis(n-
butylcyclopentadienyl)zirconium hydridochloride, bis(n-
butylcyclopentadienyl)hafnium hydridochloride,
bis(p ntam thylcyclopentadienyl)zirconium dichloride,
35   bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-
butylcyclopentadienyl)zirconium dichloride,

cyclopentadienyl-zirconium trichloride,
bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-
indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-
tetrahydro-1-indenyl)] zirconium dichloride. The

5   metallocene compounds utilized within the embodiment of
this art can be used as crystalline solids, as solutions in
aromatic hydrocarbons or in a supported form.

     The alumoxane can be impregnated into the carrier at
any stage of the process of catalyst preparation. In this

10   embodiment, the amount of Al, provided by alumoxane, is
sufficient to provide an Al:transition metal (provided by
metallocene) mole ratio ranging from 50 to 500, preferably
75 to 300.

     The class of alumoxanes comprises oligomeric linear

15   and/or cyclic alkylalumoxanes represented by the formula:
$R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear alumoxanes and
$(-Al(R)-O-)_m$ for oligomeric cyclic alumoxane
wherein n is 1-40, preferably 10-20, m is 3-40, preferably
3-20 and R is a C_1-C_8 alkyl group and preferably methyl.

20   MAO is a mixture of oligomers with a very wide distribution
of molecular weights and usually with an average molecular
weight of 1200. MAO is typically kept in solution in
toluene. The MAO solutions remain liquid at fluid bed
reactor temperatures.

25   Incorporation of the activated metallocene component
onto the carrier can be accomplished in various ways.
Incorporation of either or both the alumoxane and the
metallocene component can be into the slurry resulting from
the addition, i.e. after the addition, of the non-

30   metallocene transition metal.

     Alternatively, and in accordance with the unique
method of infusion of alumoxane into the pores of the
carrier, the carrier slurry can be stripped of solvent,
after the addition of the non-metallocene transition metal

35   compound, to form a free-flowing powder. The free flowing
powder can then be impregnated by determining the pore

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volume of the carrier and providing an alumoxane (or
metallocene-alumoxane) solution in a volume equal to or
less than the total pore volume of the carrier, and
recovering a dry catalyst precursor. The resulting free-
5   flowing powder, referred to herein as a catalyst precursor,
is combined with an activator (sometimes referred as a
cocatalyst).

       The volume of the solution comprising a solid
alumoxane and a solvent therefor can vary. In a preferred
10   embodiment, of alumoxane incorporation into the carrier,
one of the controlling factors in the alumoxane
incorporation into the carrier material catalyst synthesis
is the pore volume of the silica. In this preferred
embodiment, the process of impregnating the carrier
15   material is by infusion of the alumoxane solution, without
forming a slurry of the carrier material, such as silica,
in the alumoxane solution. The volume of the solution of
the alumoxane is sufficient to fill the pores of the
carrier material without forming a slurry in which the
20   volume of the solution exceeds the pore volume of the
silica; accordingly and preferably, the maximum volume of
the alumoxane solution is, does not exceed, the total pore
volume of the carrier material sample. That maximum volume
of the alumoxane solution insures that no slurry of silica
25   is formed. Accordingly, if the pore volume of the carrier
material is 1.65cm^3/g, then the volume of alumoxane will be
equal to or less than 1.65 cm^3/gram of carrier material.
As a result of this proviso, the impregnated carrier
material will appear dry immediately following impregnation
30   although the pores of the carrier will be filled with <u>inter
alia</u> solvent.   Solvent may be removed from
the alumoxane impregnated pores of the carrier material by
heating and/or under a positive pressure induced by an
in rt gas, such as nitrogen. If mploy d, the conditions
35   in this step are controlled to reduce, if not to eliminate,
agglomeration of impregnated carrier particles and/or

crosslinking of the alumoxane. In this step, solvent can be removed by evaporation effected at relatively low elevated temperatures of above 40°C and below 50°C to obviate agglomeration of catalyst particles and

5   crosslinking of the alumoxane. Although solvent can be removed by evaporation at relatively higher temperatures than that defined by the range above 40°C and below 50°C, short heating times schedules must be employed to obviate agglomeration of catalyst particles and crosslinking of the

10   alumoxane.

       In a preferred embodiment, the metallocene is added to the solution of the alumoxane prior to impregnating the carrier with the solution. Again, as noted above, the maximum volume of the alumoxane solution also including the

15   metallocene is the total pore volume of the carrier material sample. The mole ratio of alumoxane provided aluminum, expressed as Al, to metallocene metal expressed as M (e.g. Zr), ranges from 50 to 500, preferably 75 to 300, and most preferably 100 to 200. An added advantage of

20   the present invention is that this Al:Zr ratio can be directly controlled. In a preferred embodiment the alumoxane and metallocene compound are mixed together at a temperature of 20 to 80°C, for 0.1 to 6.0 hours, prior to use in the infusion step. The solvent for the metallocene

25   and alumoxane can be appropriate solvents, such as aromatic hydrocarbons, halogenated aromatic hydrocarbons, ethers, cyclic ethers or esters, preferably it is toluene.

       The catalyst precursor component formed from the organomagnesium compound, the non-metallocene transition

30   metal and the activated metallocene, must now be activated with a cocatalyst, which is an alkyl aluminum compound, free of water and free of oxygen-containing oligomers.

       The cocatalyst can be a trialkylaluminum, free of an alumoxane. Preferably, trimethylaluminum (TMA) is the

35   cocatalyst or activat r. The amount of the TMA activat r is sufficient to give a TMA:Ti molar ratio f 10:1 to

1000:1, preferably 15:1 to 300:1, and most preferably 20:1
to 100:1. The catalyst exhibits high activity for long
periods of time, and exhibits little deactivation.

5   The catalyst precursor of this invention comprises a
metallocene compound and an alumoxane which is fed to the
fluid bed reactor for gas phase polymerizations and
copolymerizations of ethylene in particulate form.
Moreover, in accordance with the invention, the cocatalyst
or activator is fed to the fluid bed reactor for
10   polymerizations and copolymerizations of ethylene in the
absence of alumoxane solution.

                              EXAMPLES

(I)   CATALYST PREPARATION

         The examples of catalyst preparation are from
15   copending application, S.N. 08/151664, filed November 15,
1993:

         The titanium component of the catalyst was prepared
first and isolated as a free-flowing powder. The zirconium
component of the catalyst was prepared using a "dry"
20   impregnation method described above.

Example 1

         (A) Titanium Catalyst Component Preparation. 541
grams of Davison grade 955-[600°C calcination temperature]
silica was weighed into a two-gallon stainless steel
25   autoclave containing a stirring paddle. Next, ca. 4.8
liters of dry isopentane was added to the autoclave and the
stirring rate was set at 100 rpm. The temperature of the
silica/isopentane slurry was 54-58°C. Next, 546 mls of
dibutylmagnesium (0.713 mmol/ml) was added to the slurry.
30   The contents of the autoclave were stirred for 60 minutes.
Then, 33.8 mls of neat 1-butanol were added and stirring
was continued for one hour. Finally, 23.5 mls of titanium
tetrachloride was added to the autoclave and stirring
continued for 60 minutes. After this time, all solvents
35   were removed by evaporation under a nitrogen purge.

19

Catalyst yield was 496 grams of a tan free-flowing powder.
Ti found 1.56 wt.%; Mg found 1.45 wt.%.

Example 2 Titanium/Zirconium Catalyst Preparation

Solution B: 12.95 grams of (BuCp)$_2$ZrCl$_2$ was transferred
5   to a one-liter bottle and 687 ml of a 4.67 Molar (13.7 wt.%
Al) solution of methylalumoxane were added. The bottle was
shaken for one minute to form a yellow solution which was
transferred into a 1.5 liter stainless steel hoke bomb and
used immediately as described below.

10   Under an inert atmosphere, 401 grams of the titanium-
containing catalyst described above [(A) Titanium Catalyst
Component Preparation] was added to a 2-gallon, glass-
reactor vessel containing a helical stirrer to agitate the
catalyst powder and a temperature jacket which was set at
15   30°C. The stirrer was set at 125 rpm. Then, the contents
of the hoke bomb (solution B) was added to the titanium-
containing catalyst in approximately 5-10 ml aliquots every
30-60 seconds over a 45 minute period. The total volume of
solution (B) used was such that the titanium containing
20   catalyst always appeared "dry" during the entire addition
time. However, during this addition time, the light tan
titanium-containing catalyst turned a dark brown color.
After the addition of solution (B) was complete, the jacket
temperature was set at 45°C and the residual toluene was
25   removed with a nitrogen purge for 5 hrs. After this time
the catalyst was a dark brown free-flowing powder.
Analytical results: Mg, 0.99 wt.%; Ti, 1.14 wt.%; Al, 13.0
wt.% and Zr, 0.42 wt.%.

Example 3

30   A series of resins produced with the catalyst
described in U.S. 5,332,706 (catalyst of Example 3) and the
catalyst of Example 2. The resins were characterized for
their dynamic rheological characteristics (viscosity and
elasticity) using the RMS 800 rheometer using ASTM D44440-
35   84. The granular resins were melt homogenized with
adequate quantities of anti-oxidant bef re measurement were

conducted at 200°C. These resins were produced under a
variety of process conditions resulting in a broad range of
viscosities. It is clear from the attached plot that at a
given low shear viscosity (@ 0.1 sec^{-1}), the resins produced
5   with the Example 2 catalyst have lower elasticity (ratio of
storage modulus G' over loss modulus G" @ 0.1 sec^{-1}) than
the corresponding resin catalyzed by the catalyst of U.S.
Patent 5,332,706. This difference in the elasticity is
attributed to the use of a different type of the Ti
10   catalyst component for producing the HMW component. It is
apparent that the HMW component produced by the Example 2
catalyst component is narrower in MWD (lower elasticity)
than that produced by the component disclosed in U. S.
Patent 5,332,706. The resin of the invention produced by
15   the catalyst of Example 2 above can be described by the
following equation:

    Elasticity (G'/G") @ 0.1 sec^{-1} < .44 + 10^{-7} x (Viscosity
@ 0.1 sec^{-1})

    The lower elasticity of the resins provides a distinct
20   advantage in terms of bubble stability as illustrated in
the following example.

Example 4

In this example we compare the processability of a HMW-HDPE
resin (Resin B) produced by the catalyst of Example 2 to
25   that of the resin produced by the catalyst of Example 3 in
U.S. Patent No. 5,332,706 (Resin A). The granular resin A
had an average particle size of 0.024 inch and a Ti residue
of 6.3 ppm. In comparison, granular resin B had an average
particle size of 0.018 inches and a Ti residue of 14.6 ppm.
30   The resins were compounded on a Banbury unit. The bubble
stability of the resins is measured in terms of the ability
to produce a 1 mil film on a 50 mm Alpine extruder equipped
with a 100 mm due (1 mm die gap) at an output rate of 120
lbs/hr, BUR of 4 and neck height of 28 inches. The resin
35   characteristics and processabilities were as follows:

Property	Resin A	Resin B
Catalyst	Example 3 in U. S. 5,332,706	Example 2
FI	8.0	7.1
MFR	154	108
Base resin rheology:		
Viscosity @ 0.1 1/sec., 100,000 poises	11.8	9.5
Elasticity (G'/G") @ 0.1 sec^{-1}	.61	.51
Is (G'/G")0.1 < (10^{-7} x V0.1) + 0.44	No	Yes
Produce 1 mil film @ 120 lbs/hr	No	Yes

The invention resin B had good bubble stability and
lower elasticity compared to the resin produced with the
prior art catalyst.

Example 5

The films produced from the invention resins possessed
excellent properties as illustrated in this example. The
resin was produced in the fluid bed reactor under the
following conditions: reactor temperature 90°C, P_E 189
psig, iC5/C2 = .17, H2/C2 = .011, C6=/C2= .013, TMA 218 ppm
and a residence time of 3-3.5 hours. The catalyst based on
the Example 1 synthesis of the Ti component was formed with
the alcohol addition step. The FI and MFR of the resin was
6.6 and 110, respectively. The base resin elasticity and
viscosity at .1 sec-1 were .53 and 10^6 poises,
respectively. The film was blown on the Alpine extruder at
120 lbs/hr, 4:1 BUR, and 28 inch neck-height. The
excellent bubble stability of the resin allowed us to

produce film at both 1 and 0.5 mils. The film properties
were as follows:

Gauge, mils	Dart Impact, F50 g	MD/TD Elmendorf Tear, g/mil
1.0	444	26/206
0.5	426	20/60

Thus it is apparent that there has been provided, in
accordance with the invention, a product that fully
satisfies the objects, aims, and advantages set forth
above. While the invention has been described in
conjunction with specific embodiments thereof, it is
evident that many alternatives, modifications, and
variations will be apparent to those skilled in the art in
light of the foregoing description. Accordingly, it is
intended to embrace all such alternatives, modifications,
and variations as fall within the spirit and broad scope of
the appended claims.

<u>CLAIMS</u>:

        1.   A product in the form of particles, characterized by a weight average particle diameter in the range of 0.01 to 0.04 inches,

5   each particle comprising a resin which is selected from the group consisting of homopolymer or copolymer of ethylene,

                  wherein the resin has a density of 0.89 to .97; has a Mw/Mn of 2.5 to 60, and has FI of 1 to 100, wherein said resin comprises two components of

10   different molecular weight, wherein one of said two components is a high molecular weight component (HMW) and wherein another of said two components is a low molecular weight component (LMW) with a molecular weight less than that of

15   HMW;

                  wherein the LMW component is produced by a metallocene transition metal catalyst component and has a narrower molecular weight distribution than the HMW component which is produced by a

20   non-metallocene transition metal catalyst component;

                  wherein the resin is formed in situ in a single reactor by a catalyst comprising a source of a metallocene transition metal;

25   wherein the resin has dynamic rheological properties which satisfy the following equation:

Elasticity (G'/G") G0.1 sec^{-1} < 0.44 + 10^{-7} x (viscosity @ .1 sec).

        2.   The product of Claim 1, wherein the resin has a

30 density which ranges from .930 to .970 g/cc.

        3.   The product of Claim 1, wherein the resin has a specific density which ranges from .940 to .970.

4. The product of Claim 1, wherein the resin has a specific density which ranges from .930 to .940.

5. The product of Claim 1, wherein the Mw/Mn ranges from 10 to 40.

6. The product of Claim 1, wherein the Mw/Mn ranges from 15 to 30.

7. The product of Claim 1, which is crosslinkable.

8. The product of Claim 1 which is a homopolymer of ethylene.

9. The product of Claim 1 which is a copolymer of ethylene and an alpha olefin of 3 to 10 carbon atoms.

10. The product of Claim 1 which is a copolymer of ethylene and an alpha olefin of 4 to 8 carbon atoms.

11. The product of Claim 1 which is a copolymer of ethylene and an alpha olefin which is selected from the group consisting of propylene, 1-butene, 1-hexene, 1-octene, 4-methyl-pentene and admixtures thereof.

12. The product of Claim 1 which is a copolymer of ethylene and 1-hexene.

13. The product of Claim 12, wherein 0 to 20 weight percent of alpha olefin pf 4 to 8 carbon atoms.

14. The product of Claim 1 wherein the resin contains 0.1 to 10 ppm of said metallocene transition metal.

15. The product of Claim 19, wherein the resin contains 1 to 30 ppm titanium.

16. The product of Claim 1, wherein the resin has a specific density in the range of 0.918 to 0.929.

17. The product of Claim 1, wherein the low molecular weight component is characterized by M_w/M_n of less than 3.
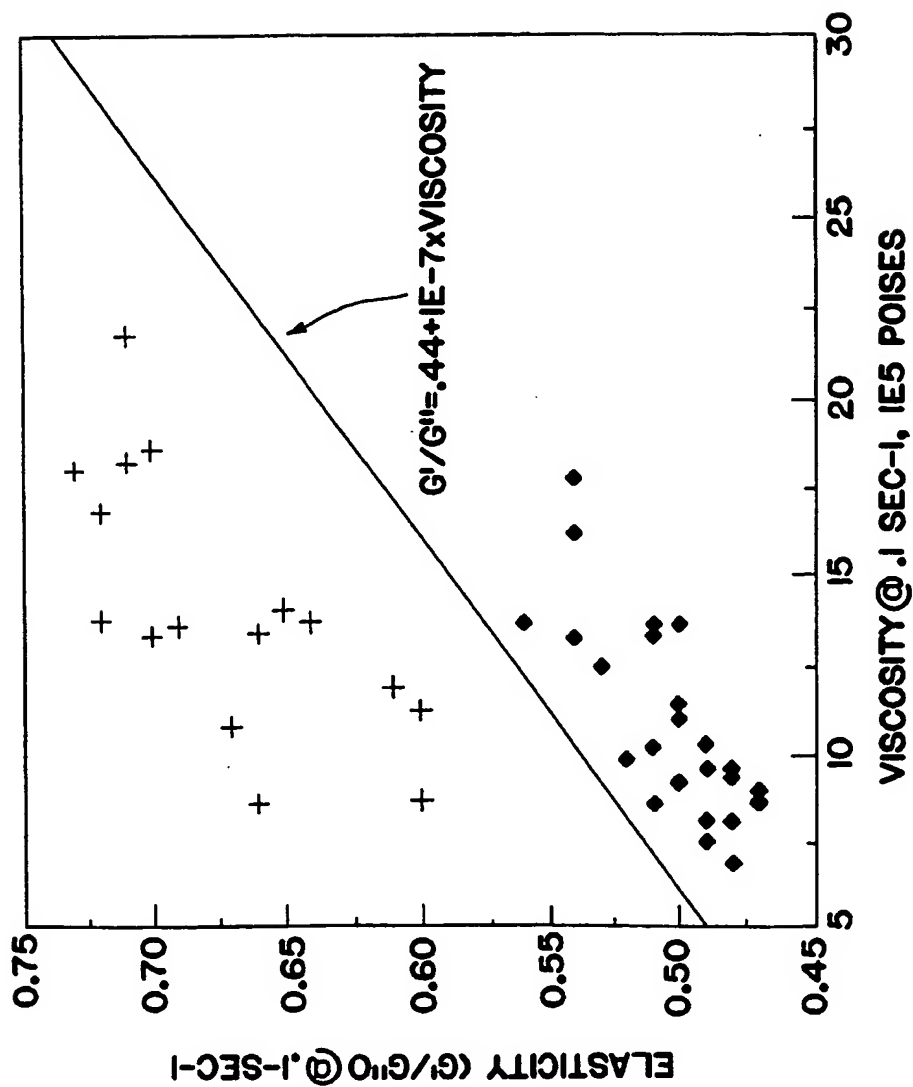
5

18. The product of Claim 1, wherein the high molecular weight components characterized by M_w/M_n of greater than 3.

19. The product of Claim 17, wherein the high molecular weight components characterized by M_w/M_n of

10   greater than 3.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/06182

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6)   :Please See Extra Sheet.
US CL   :428/35.7; 502/103, 114; 526/148, 153

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/35.7; 502/103, 114; 526/148, 153

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

NONE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,918,038 (SAMUELS ET AL.) 17 April 1990, col. 5, lines 30-43.	1-15
Y	US, A, 5,032,562 (LO ET AL.) 16 June 1991, col. 1, lines 64-67.	1-15

☐ Further documents are listed in the continuation of Box C.   ☐   See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	
"E"	earlier document published on or after the international filing date	"X"	document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	
"P"	document published prior to the international filing date but later than the priority date claimed	"&"	document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 AUGUST 1996	27 AUG 1996

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A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

C08F 4/64, 4/44; C08L 23/00